Available online at www.sciencedirect.com

SciVerse ScienceDirect

Acta Materialia 60 (2012) 5601–5614

Acta MATERIALIA

www.elsevier.com/locate/actamat

Structure, phase stability and elastic properties in the $Ti_{1-x}Zr_xN$ thin-film system: Experimental and computational studies

G. Abadias [a,*], V.I. Ivashchenko [b], L. Belliard [c], Ph. Djemia [d]

[a] *Département Physique et Mécanique des Matériaux, Institut P', UPR 3346, CNRS-Université de Poitiers-ENSMA, SP2MI, Téléport 2, F86962 Futuroscope-Chasseneuil, France*

[b] *Institute of Problems of Material Science, NAS of Ukraine, Krzhyzhanovsky Str. 3, 03142 Kiev, Ukraine*

[c] *UPMC-Institut des NanoSciences de Paris, 4 Place Jussieu, 75252 Paris Cedex 05, France*

[d] *Université Paris 13, Sorbonne Paris Cité, Laboratoire des Sciences des Procédés et des Matériaux, CNRS, F-93430 Villetaneuse, France*

Received 6 March 2012; received in revised form 27 June 2012; accepted 4 July 2012
Available online 15 August 2012

Abstract

The composition-dependence of the structure and elastic properties of ternary $Ti_{1-x}Zr_xN$ alloys is systematically investigated by combining thin film growth and ab initio calculations. Single-phase $Ti_{1-x}Zr_xN$ thin films ($0 \leqslant x \leqslant 1$) with a rocksalt structure have been deposited using dc reactive magnetron sputtering at $T_s = 300$ °C in Ar/N_2 plasma discharges. The structure, stress state and phase stability upon thermal annealing were studied by X-ray diffraction (XRD), while the acoustic and elastic properties were measured using Brillouin light spectroscopy, picosecond ultrasonics and nanoindentation. First-principles pseudopotential calculations of the total energy, lattice constants, bulk modulus, and single-crystal elastic constants C_{ij} for several cubic ordered structures of $Ti_{1-x}Zr_xN$ alloys were also carried out. The positive values of the computed formation energies indicate that the homogeneous $Ti_{1-x}Zr_xN$ alloys can be only stabilized at high temperatures. However, the magnetron-sputtered thin films were found to retain their as-grown single-phase cubic structure during post-deposition annealing at 850 °C for 3 h. The calculated equilibrium lattice parameters are in good agreement with the stress-free lattice parameters a_0 determined experimentally from XRD using the $\sin^2\psi$ method: they both exhibit a positive deviation from Vegard-like linear interpolation. The calculated bulk modulus, elastic constants and Poisson's ratio gradually decrease from TiN to ZrN. These computed values were used to interpret the experimentally derived elastic constants and Young's modulus as functions of composition.

Keywords: Transition metal nitrides; Structure; Elastic properties; Ab initio calculations; Thin films

1. Introduction

Transition metal nitride (TMN) thin films are nowadays largely used in various applicative fields of technological importance, such as protective hard coatings for cutting tools [1–3], diffusion barriers or metallization layers in integrated circuits [4–6], growth templates for group III-nitride semiconductor devices [7,8], antibacterial overlayers for medical equipment [9] or reflecting back contacts in solar cells [10,11]. In order to improve further the functional properties of these materials, the current research strategy is driven by the prospects of synthesizing new ternary or multinary systems, by means of alloying different metal or non-metal elements [12–26]. Physical vapor deposition techniques, and especially magnetron sputter deposition, have proven to be a versatile, environment-friendly and industrially scalable route to grow such engineered materials. By adjusting the process parameters (e.g. substrate temperature, working pressure, bias voltage) and tuning the film composition, a wide range of microstructures, including metastable substitutional solid solutions, dual-phase nanocomposites and amorphous alloys, can be tailored in these multi-component systems [27–33].

* Corresponding author.
E-mail address: gregory.abadias@univ-poitiers.fr (G. Abadias).

1359-6454/$36.00 © 2012 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.actamat.2012.07.014

Along with other TMNs, the TiN–ZrN system has attracted considerable interest due to the high hardness, relatively high electrical conductivity, chemical inertness and gold-like color of the constitutive binary nitrides [34], as well as potential use as an inert matrix for future gas-cooled fast reactors [35]. Several studies have been reported on the structural and mechanical properties [36–44], residual stress [45–48] as well as wear-resistance [49] of (Ti,Zr)N alloys. However, limited information is available regarding the phase stability and elastic properties of these ternary alloys. Early works by Holleck [27] predicted a relatively large miscibility gap between the two components with a critical temperature of ~2000 °C, below which a phase separation takes place through spinodal decomposition for ZrN-rich alloys [50]. Recently, using ab initio calculations for cubic [NaCl-structure] $Ti_{1-x}Zr_xN$ alloys, Hoerling et al. [44] computed a pseudo-binary TiN–ZrN phase diagram, which exhibits a miscibility gap closing at 5000 K. Experimentally, they found that single-phase $Ti_{1-x}Zr_xN$ thin films with a rocksalt structure deposited by a cathodic arc were stable up to 1200 °C and that the relationship between lattice parameter and Zr content was roughly linear, resembling a Vegard-like behavior. However, positive deviations from linear interpolation between TiN and ZrN cell sizes were reported for sputtered $Ti_{1-x}Zr_xN$ films [50]. The structure, electronic and bonding properties of a large variety of Ti_xMe_{1-x} nitrides (Me = Zr, Nb, Ta, Hf, Mo, W) were also reported by Matenoglou et al. [13]. Although a global Vegard-like linear concentration dependence was observed for all investigated systems, small deviations from linearity were evidenced in the variation of the interplanar spacings vs. Ti content and ascribed to growth-dependent stresses. Therefore, a careful characterization of the strain–stress state using X-ray diffraction (XRD) is required to appropriately separate elastic strain and chemical contributions to the measured lattice parameters and therefore ascertain conclusions on the validity of Vegard's empirical rule. It has been shown previously that a direct determination of the "stress-free lattice parameter" a_0 solely linked to chemical effects was possible thanks to additional stress data obtained on annealed samples [46,51].

The knowledge of elastic properties of $Ti_{1-x}Zr_xN$ alloys is of importance to study their mechanical behavior as well as to relate XRD elastic strain to stress using linear elasticity theory. For binary TiN and ZrN compounds, values of bulk modulus B, Young's modulus E, Poisson ratio ν, as well as single-crystal elastic constants C_{ij} are well documented, though reported literature data are somewhat scattered [51–54]. For metastable $Ti_{1-x}Zr_xN$ alloys, E and B data have been computed from ab initio calculations [44,55,56]; however, to the best of our knowledge, no experimental or theoretical C_{ij} data are available in the literature.

In the present paper, we investigate the structure, stability and elastic properties of $Ti_{1-x}Zr_xN$ alloys in the whole compositional range ($0 \leqslant x \leqslant 1$) by combining experiments on thin films grown by dc reactive magnetron sputtering and modeling of ordered compounds using first-principle calculations. The evolution of the lattice parameter of as-deposited and annealed films with ZrN content was determined using XRD, while the shear (C_{44} elastic constant), the longitudinal (C_{33} elastic constant) and Young's moduli E were obtained from Brillouin light scattering (BLS), picosecond ultrasonics (PU) and nanoindentation, respectively.

2. Experimental details and computational approach

2.1. Film growth

A series of $Ti_{1-x}Zr_xN$ films were deposited at $T_s = 300$ °C on Si substrates using dc reactive magnetron sputtering in a high vacuum chamber pumped down to $\sim 2 \times 10^{-6}$ Pa using a cryogenic pump. The deposition system uses a confocal geometry in which the substrate holder is mounted on a rotating and heating stage over three 75 mm diameter, water-cooled planar magnetrons oriented 25° from the substrate normal and at a mean target-to-substrate distance of 18 cm. Prior to deposition, Ti (99.995% purity) and Zr (99.2% purity) targets were pre-sputtered for 5 min under Ar plasma discharge to remove any possible surface oxides or contaminants. Then, ternary $Ti_{1-x}Zr_xN$ thin films were deposited using a dc plasma discharge from an $Ar + N_2$ gas mixture. The magnetrons were operating in unbalanced mode and a negative substrate bias of –60 V was applied to the substrate during deposition using a 3 W rf power supply. The ZrN fraction in the films was monitored by adjusting the respective power of the Ti and Zr targets, while sputtering occurred in metallic mode and at a fixed working pressure of 0.19 Pa [57]. Substrates were rotated at 10 rpm to obtain homogenous films. The total film thickness was adjusted to $t \sim 300$ nm for all samples, according to the deposition rates (in the 0.14–0.38 nm s^{-1} range) deduced from X-ray reflectivity (XRR) measurements on reference samples, as reported elsewhere [57].

The elemental composition was determined using energy-dispersive X-ray spectroscopy (EDX) combined with Rutherford backscattering spectroscopy (RBS). The N content, deduced from RBS analysis, was found to vary between 45 and 51 at.%. Taking into account the uncertainty limit of the RBS technique (±5%), we will consider in the following the ternary nitride films as stoichiometric, and refer to the quantity $x = Zr/(Zr + Ti)$ to denote the samples.

Post-deposition thermal annealing at 850 °C for 3 h was performed in a quartz tube furnace, pumped down to 3×10^{-4} Pa using a turbomolecular pump.

2.2. X-ray diffraction

The crystal structure and preferred orientation of as-deposited and annealed $Ti_{1-x}Zr_xN$ films were determined